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(21) International Application Number: PCT/NO99/00192 (22) International Filing Date: 11 June 1999 (11.06.99) (30) Priority Data: 19983156 8 July 1998 (08.07.98) NO (71) Applicant (for all designated States except US): NORSK HYDRO ASA [NO/NO]; N-0240 Oslo (NO). (72) Inventors; and (75) Inventors/Applicants (for US only): OBRESTAD, Torstein [NO/NO]; Helgja, N-3745 Ulefoss (NO). MOLAND, Lars, Gustav [NO/NO]; Hovetbakken 2, N-3927 Porsgrunn (NO). (74) Agent: JOHNSEN, Venche, Høines; Norsk Hydro ASA, N-0240 Oslo (NO).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: METHOD FOR MANUFACTURING A CALCIUM NITRATE MELT AND PRODUCTS THEREOF (57) Abstract The invention relates to a method for manufacturing a homogeneous and ammonium free calcium nitrate melt with high solidification temperature, suitable for conventional particulation methods, by mixing a potassium source with a calcium nitrate source and heating the formed mixture to 150–155 °C for forming a melt comprising 1.5–5.5 % by weight of K (as KNO ₃), 13–18 % by weight of water and 70–80 % by weight of Ca(NO ₃) ₂ . The invention further relates to homogeneous and ammonium free calcium nitrate particles where the particles are a particulated product from a melt comprising 1.5–5.5 % by weight of K (as KNO ₃), 13–18 % by weight of water and 70–80 % by weight of Ca(NO ₃) ₂ .		

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Method for manufacturing a calcium nitrate melt and products thereof

The present invention relates to a method for manufacturing a homogeneous and ammonium free calcium nitrate melt with high solidification temperature suitable for conventional particulation methods. The invention further comprises products of such melt.

Today pure $\text{Ca}(\text{NO}_3)_2$ (abbreviated as CN) is commercially available as crystalline products, mainly $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and as aqueous solutions containing 45-50% $\text{Ca}(\text{NO}_3)_2$.

Aqueous CN products have high handling costs in addition to containing much water. Consequently, the logistic costs on nutrient basis are rather high.

The crystalline products have poor handling properties with high caking tendency, high dust content and low melting point ($43\text{-}50^\circ\text{C}$). Thus CN crystals are not suitable for bulk handling.

Due to low solidification temperature ($43\text{-}50^\circ\text{C}$) and undercooling, it is extremely difficult to obtain pure CN particles from a CN melt by using traditional particulation methods as granulating or prilling.

To improve the solidification property and avoid undercooling NH_4NO_3 (abbreviated as AN) has been added to the melt.

Today Norsk Hydro's solid calcium nitrate product; NH-CN, contains 6-8% by weight AN, 15% by weight of crystalline water and 77-79% by weight of $\text{Ca}(\text{NO}_3)_2$.

For some applications, however, the NH_4 -content in the calcium nitrate product is a significant disadvantage. For instance as setting accelerator in concrete where NH_4 reacts to NH_3 -gas, and for some agronomic applications.

From the Norwegian patent application NO 954336 it is known NK fertilisers containing 55-85% KNO_3 (abbreviated as KN) and 14-40% $\text{Ca}(\text{NO}_3)_2$ and a method for manufacturing these fertilisers.

The product range covered in this application was intended to be a complementary fertiliser in the pure KNO_3 market. Sufficient solidification properties and particle strength were obtained by evaporating the melt to a very low water content (0.5-6%). Hence, the physical properties and the process requirements as evaporation and particulation parameters, for the melts covered in NO 954336 were quite different from those according to the present invention.

Another objective of the invention according to NO 954336 was to make a fertiliser rich in K that could be blended mechanically with NH-CN to cover the range from 0-33% K. Consequently, all the grades containing less than 21% K will be mechanical mixtures, containing NH_4 from the regular CN. Mechanical mixtures with low K-content contain almost the same amount of NH_4 as regular NH-CN, making them unsuitable for the earlier mentioned applications. The products according to the present invention are homogeneous that contain no NH_4 .

NO 954336 describes a homogeneous NK product containing 55-85% of KN contrary to the product according to the present invention which basically is a CN product containing minor amounts of KN and with no NH_4 .

The main object of the invention was to arrive at a complementary calcium nitrate product to the crystalline and liquid $\text{Ca}(\text{NO}_3)_2$ product.

Another object of the invention was to arrive at a homogeneous and ammonium free calcium nitrate in granular or prilled form.

A further object of the invention was to arrive at a homogeneous and ammonium free calcium nitrate in granular form with good handling and storage properties.

The inventors have been investigating different ways of substituting the ammonium content in NH-CN without reducing the quality of the product.

Furthermore, it was important that the new CN melt had good solidification properties to utilise conventional particulation processes as granulation or prilling. This demands that

the melt is not undercooling too much, and that the solidification temperature is reasonable high.

In the present invention a melt is defined to be an aqueous solution containing not more than 22 % water.

The inventors found that homogeneous CN particles with excellent properties were obtained when the NH_4 -content in NH-CN was replaced with a potassium source in a certain concentration. This replacement raises the solidification temperature of the melt from 43-50°C (for a pure CN melt) to 85-90°C (for a (CN+K) melt) making it suitable for conventional particulation processes as granulation and prilling.

The CN melt was manufactured by mixing the potassium source with a calcium nitrate source. An aqueous $\text{Ca}(\text{NO}_3)_2$ -solution is suitable as a calcium nitrate source. Potassium nitrate (KNO_3) in a solid or aqueous form is suitable as a K-source. Another alternative potassium source is KOH neutralised with nitric acid.

Prior to the conventional particulation, the water content in the melt was adjusted by evaporation.

Furthermore, it was found that undercooling was avoided and particulation with conventional methods was possible when the CN melt had a certain concentration range of K, water and CN. This range is defined as follows:

1.5 - 5.5 % by weight of K (as KNO_3)

13 - 18 % by weight of water

70 - 80 % by weight of $\text{Ca}(\text{NO}_3)_2$

In view of these findings particulation of melts within the above mentioned ranges were performed.

Granulation tests were carried out in a pilot scale pan granulator, with good results. Layering was obtained as the dominating particle growth mechanism with a granulation temperature of 84°C. The particles from the granulator were of nice spherical shape, and the crushing strength of 2.8 mm particles were 3-5 kg. No caking or post reactions occurred during cooling of the material.

The optimal composition of the melt for granulation seemed to be 74-75% $\text{Ca}(\text{NO}_3)_2$, 15-16% water and 2.5-4.0 % K.

Prilling tests were carried out with good results. Appropriate melt temperature was 90°C and, as for regular NH-CN, 1-5% seed crystals had to be mixed into the melt before prilling. The results were good for the whole concentration range but, as for granulation, the optimal composition of the melt seemed to be about the same as for particulation by granulation.

The scope of the invention and its special features are as defined by the attached claims.

The invention will now be further explained in connection with the description of the examples and the figure.

Figure 1 shows water absorption of CN with K according to the invention compared with corresponding results for regular CN with NH_4 .

Example 1

This example shows granulation of $\text{Ca}(\text{NO}_3)_2$ with 3.6% K (KNO_3 as potassium source).

94.2 weight % of 50% $\text{Ca}(\text{NO}_3)_2$ -solution was mixed with 5.8 weight % crystalline KNO_3 , and heated to 155°C, giving the melt a water content of ~15.5%.

Some of the melt was solidified and crushed to particles of 0.7-2.0 mm (d_{50} : 1.3mm). The particles were fed to a pan granulator (diameter: 24 cm) as building material. The melt was then sprayed into the granulator. Appropriate granulation temperature was ~84°C. The granulation properties of the melt were very good.

Because layering was the dominating particle growth mechanism, the visual appearance of the particles from the granulator was very good, both regarding roundness and smoothness.

The finished product from the granulator had a d50 of 2.3 mm, with a particle strength of 3-5 kg for 2.8 mm. No caking or post reactions occurred during cooling of the material.

Example 2

This example shows granulation of $\text{Ca}(\text{NO}_3)_2$ with 4.0% K (KOH as potassium source).

96.4 wt% of melted $\text{Ca}(\text{NO}_3)_2$ -crystals from the Nitrophosphate process (containing 60% $\text{Ca}(\text{NO}_3)_2$, 37% water and 3% HNO_3) + 3.6 wt% of 13M Nitric Acid (HNO_3) was mixed and neutralised to pH 5-6 with a 50% KOH-solution. The mixture was then stirred for 15 minutes to dissolve the CaO-precipitations. The mixture was heated to a temperature of $\sim 155^\circ\text{C}$ (1 atm. pressure) resulting in a water content of 15.5%. The melt was subsequently granulated according to the method in example 1. The granulation properties and product properties were similar to that obtained in example 1.

Example 3

This example shows granulation of $\text{Ca}(\text{NO}_3)_2$ with 2% K (KNO_3 as potassium source).

Melted $\text{Ca}(\text{NO}_3)_2$ -crystals from the Nitrophosphate process was neutralised to pH 5-6 with CaO. Crystalline KNO_3 was then mixed into the melt, and dissolved at 90°C . The mixture, with a Ca/K-ratio of 9.6, was heated to $\sim 153^\circ\text{C}$, resulting in a water content of $\sim 16\%$.

The melt was then cooled to 110°C , and granulated according to the same procedure as in example 1. Appropriate granulation temperature for this melt was 81°C . Except for this, the granulation properties and product properties were similar to that obtained in example 1.

Example 4

This example shows prilling of $\text{Ca}(\text{NO}_3)_2$ with 3% K (KOH as potassium source).

CaCO_3 was dissolved in 13M HNO_3 . The K-content was then adjusted with 50% KOH-solution to a Ca/K ratio of ~6.2, and the pH was adjusted to 5-6 with nitric acid. The melt was heated to 155°C, cooled to 90°C and 3% seed crystals were added, whereupon the melt was transferred to a prilling device and prilled into an oil bath. A nice product with particle strength of 5 kg for 3 mm particles was obtained.

Example 5

This example shows prilling of $\text{Ca}(\text{NO}_3)_2$ with 5% K (KNO_3 as potassium source).

76.9 wt% of 50% $\text{Ca}(\text{NO}_3)_2$ -solution was mixed with 23.1 wt% of 30% KNO_3 solution. The mixture was heated to 155°C, cooled to 90°C, added 5% seed crystals and prilled into an oil bath. Although the solidification time was somewhat higher than the melt in example 4, the prilling properties and product properties were nearly as good as that obtained in example 4.

The new homogeneous and AN free CN particles were further tested with regard to product properties as e.g. caking and water absorption.

These properties were compared with the same properties for regular CN with NH_4 . The results are shown in Table 1 and 2 and figure 1.

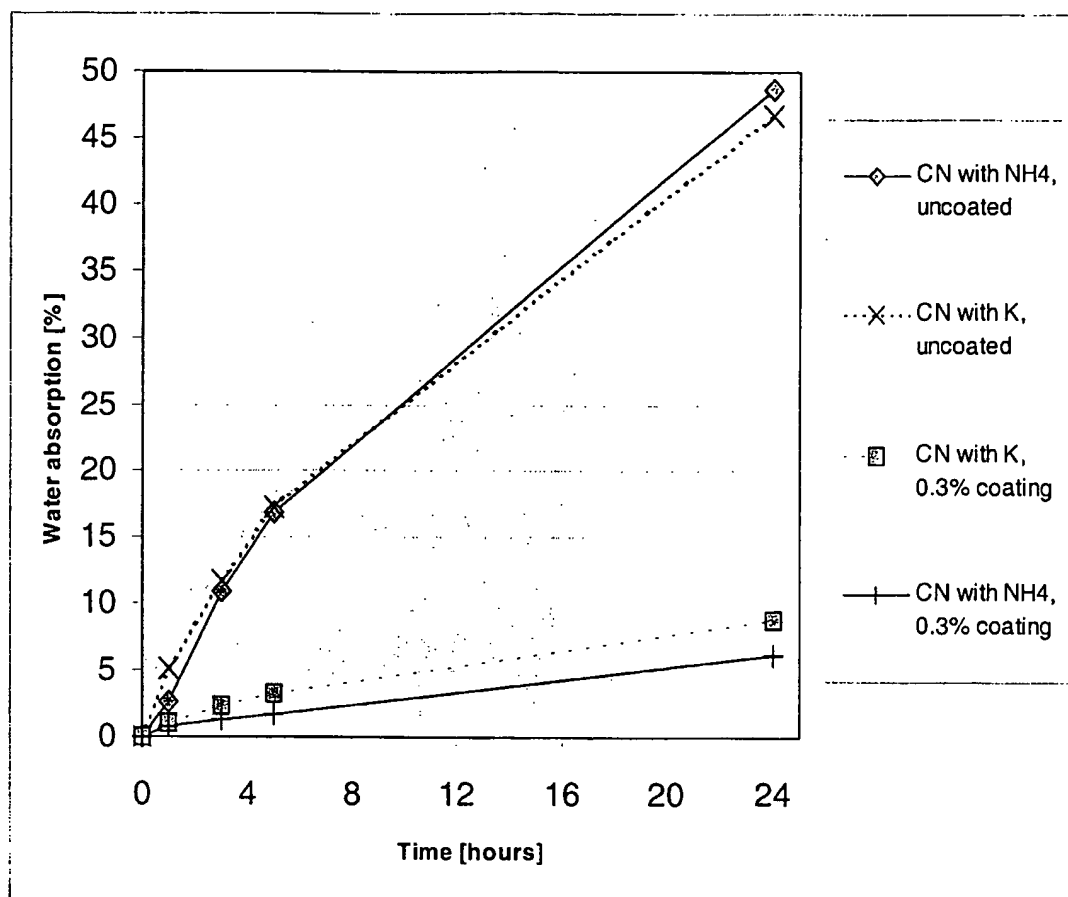


Figure 1: Water absorption at 25 °C and 70% RH.

According to figure 1, the water absorption is approximately the same for Norsk Hydro's regular CN with NH₄, and CN with K. The effect of applying 0.3% of Wax-Polymer-Oil-coating is approximately the same for CN with NH₄ and the product according to the present invention.

Table 1 :Product properties of granular NH-CN (CN+NH₄) and CN with 3.6 % K

	CN+K	CN+NH ₄
Particle strength for 2.8 mm granules	3-6 kg	3-6 kg
bulk density	1.05-1.2 kg/l	1.05-1.2 kg/l
water vapour pressure	2.5-12 mb(25 °C) (vary with water content)	2.5-12 (vary with water content)
caking tendency	very low	very low
dissolving time	easy dissolvable, rate varies with temp. and particle size	easy dissolvable, rate varies with temp. and particle size

Table 1 shows that the values for CN+K are the same as for regular CN with NH₄.

Table 2 : Physical data for CN-melts with NH₄ and K

	Regular CN with NH ₄	CN with K
T _{solidification}	90-94°C	84-88°C
Viscosity	~600 cP	600-800 cP
Crystallisation heat	~30 cal/g	~30 cal/g
Density	1.9 g/ml	1.9 g/ml

The viscosity of the melts also depends on the content of water and trace elements (impurities).

The boiling point curve is identical for CN with NH₄ and CN with K.

By applying the above procedure it will be possible to make homogeneous, NH₄-free, CN-particles with superior product properties. The product according to the invention is a complementary product to the crystalline- and liquid -market for pure Ca(NO₃)₂. The product according to the invention is free flowing, has low dust content, high melting point and high nutrient content.

Claims:

1. Method for manufacturing a homogeneous and ammonium free calcium nitrate melt with high solidification temperature suitable for conventional particulation methods, characterised by
mixing a potassium source with a calcium nitrate source and heating the formed mixture to 150-155°C for forming a melt comprising
1.5 - 5.5 % by weight of K (as KNO₃)
13 - 18 % by weight of water
70 - 80 % by weight of Ca(NO₃)₂.
2. A method according to claim 1, characterised by
mixing a potassium source with a calcium nitrate source and heating the formed mixture to 150-155°C for forming a melt comprising
2.5-4.0 % by weight of K (as KNO₃)
15-16 % by weight of water
74-75 % by weight of Ca(NO₃)₂.
3. A method according to claim 1, characterised by
using solid KNO₃ or a KNO₃ solution as a potassium source.

4. A method according to claim 1,
characterised by
using potassium hydroxide (KOH) neutralised with nitric acid
as a potassium source
5. A method according to claim 1,
characterised by
using an aqueous $\text{Ca}(\text{NO}_3)_2$ -solution or melt as a calcium
nitrate source.
6. Homogeneous and ammonium free calcium nitrate particles,
characterised in that
the particles are a particulated product from a melt comprising
1.5 - 5.5 % by weight of K (as KNO_3)
13 - 18 % by weight of water
70 - 80 % by weight of $\text{Ca}(\text{NO}_3)_2$.
7. Homogeneous and ammonium free calcium nitrate particles
according to claim 6,
characterised in that
the particles are a particulated product from a melt comprising
2.5-4.0% by weight of K (as KNO_3)
15-16 % by weight of water
74-75 % by weight of $\text{Ca}(\text{NO}_3)_2$.
8. Homogeneous and ammonium free calcium nitrate particles
according to claim 6 and 7,
characterised in that
the particles are a prilled product from the melt.

9. Homogeneous and ammonium free calcium nitrate particles according to claim 6 and 7, characterised in that the particles are a granulated product from the melt.

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INTERNATIONAL SEARCH REPORTInternational application No.
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A. CLASSIFICATION OF SUBJECT MATTER		
IPC6: C05C 5/04, C05C 5/02, C01F 11/44 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
IPC6: C05C, C01F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
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Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
WPI, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 392531 B (LONZA ELEKTRIZITÄTWERKE UND CHEMISOHE FABRIKEN AKTIENGESELLSCHAFT), 16 May 1933 (16.05.33), page 1, line 90 - line 98; page 2, line 12 - line 17; page 2, line 75 - line 96, claims 1,3	6-9
Y	page 1, line 90 - line 98; page 2, line 12 - line 17, page 2, line 75 - line 96; claims 1,3	1-5
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Y	WO 9715536 A1 (NORSK HYDRO ASA), 1 May 1997 (01.05.97), page 1, line 5 - line 14; page 5, line 1 - page 6, line 30, claims 1,3,4, abstract	1-5
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>SU 990752 A (DANILOVSKII YU S) (abstract) World Patents Index (online). London, U.K.: Derwent Publications, Ltd. (retrieved on 1999-10-27). Retrieved from: EPO WPI Database. DW198346, Accession No. 1983-819446</p> <p>-- -----</p>	1-9

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Information on patent family members

28/09/99

International application No.

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